

P. Yu. Apel', V. I. Kuznetsov,  
N. I. Zhitaryuk, and O. L. Orelovich

UDC 66.067.38.621.039

The etching of micropores 0-1000 Å in diameter in polyethylene terephthalate (PETP) films 5 and 10 μm thick irradiated with xenon ions was investigated. Ultrafilters with pore diameters from 150 to 800 Å were prepared by chemical treatment of the irradiated films with a track density of  $(2-3) \cdot 10^9 \text{ cm}^{-2}$ . An electron-microscopic study of their structure was performed. The filters with the fewest pores exhibited the greatest dispersion of diameters (~15%) due to the effect of the fine crystalline structure of the PETP. The specific efficiency of the ultrafilters with respect to distilled water was measured.

Little information has been published in the literature on nuclear filters with pore diameters of less than 0.05 μm, despite the fact that the possibility of preparing these filters has long been known [1, 2]. The detailed studies have primarily concerned the investigation of mica membranes [3-5], which cannot be widely used in practice. The use of nuclear filters with small pores in ultrafiltration processes is promising, and they are of great practical interest for this reason. The correct cylindrical shape of the pores and the homogeneity of the structure are distinctive properties of nuclear filters. The pore distribution by size exhibits very low dispersion. For Lavsan filters with pore diameters of ~0.5 μm, the distribution half-width at half of the height is several percent [6]. However, the problem of preparing filters with a highly homogeneous structure and significantly smaller pores requires separate examination.

The process of etching the track of a heavily charged particle in a polymer includes the stage of rapid dissolution of destroyed material in the center of the track and the stage of slower dissolution of intact material outside of the region of the track. These stages are characterized by rates  $V_t$  and  $V_o$ , respectively. Pores are formed as a result of etching, and their concity is determined by the ratio of the values of  $V_t$  and  $V_o$ . According to the generally used model of etching of a track in an isotropic material, the pore diameter in the narrowest segment (which determines the selective properties of the filter) is given in the first approximation by the expression

$$d = d_0 + 2V_o(t - l/2V_t) \quad (1)$$

where  $d_0$  is the diameter of the selectively etched area around the trajectory of the particle;  $l$  is the thickness of the starting film;  $t$  is the etching time. The values of  $d_0$ ,  $V_t$ , and  $V_o$  can to some degree vary from track to track as a result of the effect of many random factors: differences in the degree of crystallinity of the polymer, the presence of microimpurities, fluctuations in energy losses, the energetic inhomogeneity of the particles, etc. The thickness of the initial film is also not constant, and the angles of incidence of the accelerated ions in the polymer can be different. Assuming that the values listed above are independent variables, it is easy to find the dispersion of the diameters of the individual pores in a nuclear filter

$$S_d^2 = \left(2t - \frac{l}{V_t}\right)^2 S_{V_o}^2 + \left(\frac{\bar{V}_o l}{2V_t^2}\right)^2 S_{V_t}^2 \left(\frac{\bar{V}_o}{\bar{V}_t}\right)^2 S_l^2 + S_{d_0}^2 \quad (2)$$

Here  $S_{V_o}^2$ ,  $S_{V_t}^2$ ,  $S_l^2$ ,  $S_{d_0}^2$ ,  $\bar{V}_o$ ,  $\bar{V}_t$ ,  $\bar{l}$ , and  $\bar{d}_0$  are the dispersions and average values of  $V_o$ ,  $V_t$ ,  $l$ , and  $d_0$ . It follows from (2) that with a selectivity of etching  $V_t/V_o$ , equal to 100 for example, only one different thickness in the initial film,  $S_l \approx 1 \mu\text{m}$  [7], results in inconstancy of the pore diameters of  $\pm 100 \text{ Å}$ . To obtain identical small pores, a higher etching selec-

Joint Institute of Nuclear Research, Dubna. Translated from *Kolloidnyi Zhurnal*, Vol. 47, No. 1, pp. 3-8, January-February, 1985. Original article submitted August 8, 1983.

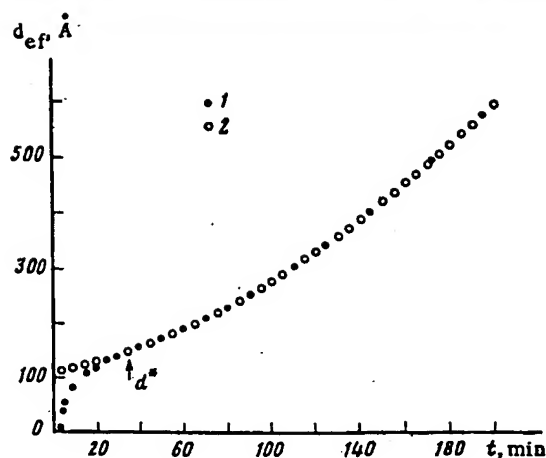


Fig. 1. Dependence of the effective pore diameter  $d_{ef}$  of a PETP film irradiated with  $^{132}\text{Xe}$  ions in 0.1 N NaOH at  $81^\circ\text{C}$  on the etching time: 1) experimental; 2) result of modeling of the pore etching process with Eq. (3) with  $V_\infty = 2.40 \text{ Å/min}$ ,  $r_0 = 54.4 \text{ Å}$ ,  $\alpha = 88.5 \text{ Å}$ .

tivity is necessary. This requirement is satisfied when the polymer film is irradiated with ions with a higher nuclear charge with subsequent sensitization of the tracks by UV irradiation [8-10] and in the corresponding etching conditions [9]. In the present article, the results of studying the process of the formation of small pores in a polyethylene terephthalate (PETP) film with chemical treatment which ensures the high selectivity of track etching and the basic properties of the prepared ultrafilters are reported.

Polyethylene terephthalate (PETP) films with a nominal thickness of  $5 \mu\text{m}$  (Khostafan) and  $10 \mu\text{m}$  (Lavsan) were used in the study. Samples of the films were irradiated with  $^{132}\text{Xe}$  and  $^{136}\text{Xe}$  ions with an energy of approximately 1 MeV/nucleon in a U-300 cyclotron at the Laboratory of Nuclear Reactions, Joint Institute of Nuclear Research. The irradiated films were stored in air and were exposed to UV light by the usual method before etching.

The kinetics of the change in the pore diameter during etching of the irradiated films was studied by a conductometric method [9, 11].

The replica method was used for the electron-microscopic studies of the structure of the nuclear ultrafilters. Scanning and photography of the replicas were performed in an EMMA-2 scanning electron microscope with accelerating voltage of 50 and 75 kV. The average pore density in the samples of the ultrafilters was determined with electron photomicrographs with a total number of pores of more than 1000. In studying the size distribution of the pores, photomicrographs of no less than three different sections of each sample were analyzed.

### 1. Etching of Small Pores

The results of the conductometric measurements of the effective pore diameter in etching of an irradiated PETP film is shown in Fig. 1. The rate of penetration of the solution along the track was calculated with the time of the appearance of through pores  $t_0$ , and the value of the radial pore etching rate  $(dr_{ef})/(dt)$  was calculated with the slope of the curve of  $d_{ef}(t)$ . The ratio of the values of  $V_t$  and  $(dr_{ef})/(dt)$  with  $r_{ef} = 75 \text{ Å}$  was  $\sim 8 \cdot 10^3$  (Fig. 1). These conditions ensure the formation of pores with very insignificant conicity. The curves of  $d_{ef}(t)$  for films of different thicknesses are qualitatively and quantitatively similar. The stage of a rapid increase in the effective pore diameter to  $\sim 150 \text{ Å}$  begins at time  $t_0$ . The bending point  $d^*$  apparently determines the boundary of the destroyed region around the course of the  $^{132}\text{Xe}$  ion. A further increase in the pore diameter takes place due to the dissolution of the undamaged polymer. The radial etching rate in this stage is not constant and increases with an increase in the pore diameter, approaching some value of  $V_\infty$ . The pore radius  $r_{ef}$  as a function of the etching time can be described by the equation

$$\frac{dr_{ef}}{dt} = V_\infty e^{-\alpha/r_{ef}} \quad (3)$$

in the initial condition  $r_{ef}(t_0) = r_0$ ;  $\alpha$  is some parameter which has the dimensionality of length. A similar mechanism was observed in [3] in etching of mica irradiated with fission fragments. The investigators in [3] correlated this effect with the fact that the curvature of the mica-solution interface changes with an increase in the pore radius, and the value of the free interphase energy (FIE) changes correspondingly. In our case, this hypothesis does not withstand quantitative testing, and the physical sense of relation [3] and parameter  $\alpha$  remains unclear. With respect to parameter  $V_\infty$ , its value actually coincides with the rate of etching of the surface of the PETP film,  $V_0$ .

### 2. Char

$\sim 100 \frac{\text{Å}}{\text{min}}$   
replica  
affect  
of the  
informa  
the sur

Th  
are sho  
replica  
1 and 2  
should  
diamete  
from th  
of the  
ular st  
and the  
dent th  
 $\mu\text{m}$ ) por

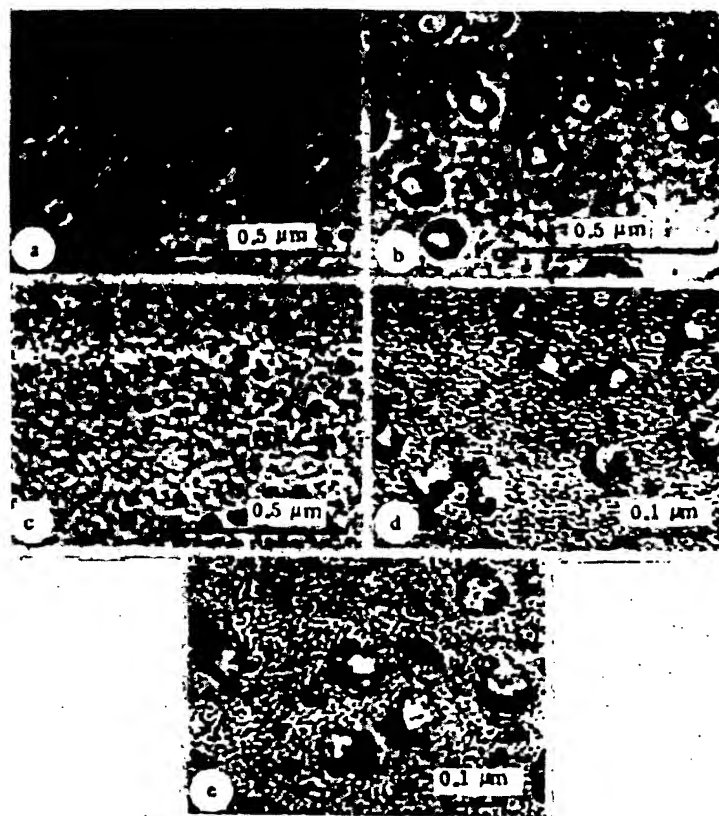


Fig. 2. Electron photomicrographs of replicas from the surface of nuclear ultrafilters: a) carbon replica, Khostafan,  $d_{ef} = 150 \text{ \AA}$ ; b) carbon replica, Lavsan,  $d_{ef} = 520 \text{ \AA}$ ; c) Au+C replica from the surface of a Lavsan ultrafilter ( $d_{ef} = 320 \text{ \AA}$ ). Gold was sputtered at an angle of  $15^\circ$  to the surface; carbon was sputtered perpendicular to the surface; Au+C replicas from the surface of Khostafan ultrafilters with  $d_{ef} = 300 \text{ \AA}$  (d) and  $d_{ef} = 520 \text{ \AA}$  (e). Sputtering was performed perpendicular to the surface.

## 2. Characteristics of the Nuclear Ultrafilters

**a. Pore Size and Pore Distribution by Size.** The precise measurement of the diameters of  $\sim 100 \text{ \AA}$  openings with the electron microscope is not a trivial task. The thickness of the replica applied to the sample is comparable to the size of the objects studied, and this can affect the results of absolute measurements even with high resolution and precise calibration of the instrument. Nevertheless, the electron photomicrographs provide valuable and graphic information on the distribution of the pores by size (dispersion) and the microstructure of the surface.

The electron photomicrographs of replicas from the surface of the nuclear ultrafilters are shown in Fig. 2. The smallest pores are completely filled with dust on application of the replicas and appear as dark spots. Their distribution by size is shown in Fig. 3 (histograms 1 and 2). Since a high value of  $V_t/V_0$  during etching ensures the absence of conicity, it should be expected that this distribution reflects the dispersion of not only the inlet pore diameters, but also the diameters inside the filter. The rms deviation of the pore diameters from the mean is 9-15%, and it decreases as the pores increase. We believe that the cause of the greater dispersion of the diameters of the small pores is the effect of the supermolecular structure of the PETP. The size of the crystallites in oriented PETP is 30-100  $\text{\AA}$  [12], and their effect on the size and shape of the smallest pores is thus great. It is also evident that supermolecular formations of this scale cannot affect the dispersion of large ( $\geq 1 \mu\text{m}$ ) pores. The nature of the supermolecular structure of PETP revealed during etching can be

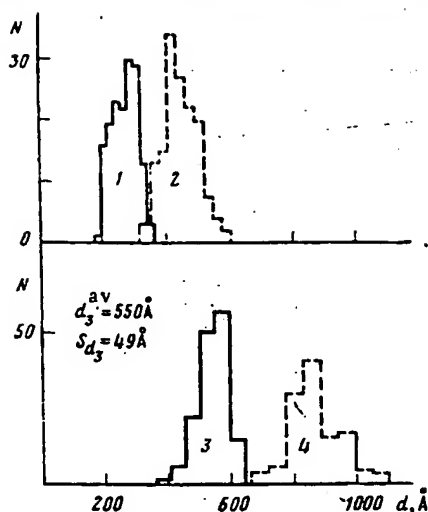


Fig. 3. Distribution of the pore diameters in Lavsan ultrafilters with  $d_{ef}$  of 200 Å (1), 330 Å (2), 520 Å (3), and 800 Å (4). Two different methods of analyzing the image are shown.

observed in Fig. 2c. A replica from the surface angle to the surface is shown here. This permitted shadowing the surface; judging by the length of the shadows, the characteristic size of the irregularities corresponds to the size of the crystallites. The microstructure of the surface of etched PETP with an average cavity size of  $\sim 100$  Å has also been found by the method of mercury porosimetry [13].

The average pore size based on the electron-microscopic data is not in precise agreement with the conductometric measurements. One of the causes of this difference could be the error due to the nonzero thickness of the replica. A second possible cause is the funnel shape of the inlet opening of the pore. The dark halos around the openings in the carbon replica in Fig. 2b are apparently evidence of this configuration; the analysis of the image in Fig. 2b shows that the average diameter of the through holes in the replica corresponds to the effective "conductometric" diameter  $d_{ef}$  with a precision of 10%, while the average diameter of the dark halos around the pores by far exceeds the value of  $d_{ef}$  (see histogram 3 in Fig. 3).

**b. Maximum Efficiency with Respect to Distilled Water.** The data on the maximum efficiency of the prepared ultrafilters are reported in Table 1. The measurements were made with no less than three samples of each rated value. Fresh distilled water was additionally purified immediately before contact with the sample by passing it through a nuclear filter with a pore diameter of 300 Å. The results obtained show that the flow of the liquid through filters with pore diameters of 300–500 Å takes place according to Poiseuille's law. A distinct quantitative correlation is observed between the structural characteristics of the filter and the flow rate of the water through the filter. In the case of smaller pore diameters, 150 and 200 Å, the flow rate of the water is lower than could be expected based on the number and geometric dimensions of the pores. The effect of surface effects apparently becomes significant in this region [13].

In this respect, the relative viscosities of the water in the pores  $\eta/\eta_0$  were calculated. The data for the different pore diameters are reported in Table 2. When the diameter decreases

TABLE 1. Characteristics of Nuclear Ultrafilters

Filter material and thickness, $\mu m$	Average pore density $n \cdot 10^{-9}$ , $cm^{-2}$	Etching time in 0.1 N NaOH, min	Predicted value of $d_{ef}$ , Å	Specific capacity with respect to distilled $H_2O$ , $\Delta P = 0.05$ MPa, $ml/sec \cdot cm^2$	Hydrodynamic pore diameter $d_h$ , Å	Bubble passage pressure $P_b$ , MPa
Khostafan, 4.7	2.1	35	150	$5 \cdot 10^{-6}$	100	$1.4 \pm 0.1$
"	2.1	108	300	$6.5 \cdot 10^{-6}$	330	$0.7 \pm 0.1$
"	2.1	174	520	$8.5 \cdot 10^{-6}$	620	$0.5 \pm 0.1$
Lavsan, 10.5	2.5	65	200	$1 \cdot 10^{-6}$	140	1.5
"	2.5	113	320	$2 \cdot 10^{-6}$	270	0.95
"	3.1	174	520	$4 \cdot 10^{-6}$	570	0.8

\*At a temperature of 19°C.

†Ethanol was used as the wetting liquid.

‡The deformation of the samples was high during testing.

TABLE 2. Relative Viscosity of Water in the Pores of Nuclear Ultrafilters with Different Diameters

$D_{\text{eff}}, \text{\AA}$	$\eta/\eta_0$	$\pm \Delta\eta/\eta_0$
150	5,5	2,1
200	4,6	1,8
320	1,5	0,7
520	0,8	0,4

from 500 to 150  $\text{\AA}$ ,  $\eta/\eta_0$  increases, and these values are higher than the corresponding values obtained for the flow of water in quartz capillaries [14, 15]. This is probably due to the specific effect of the surface of the chemically treated polymer material (polyethylene terephthalate) on the flow of water in the ultrasmall pores. However, the error in the determination of the diameter of the pores in the ultrafilters ( $\pm 10\%$ ) results in significant scattering of the experimental data. The further development of the method of measuring the pore diameters and obtaining more reliable values of  $\eta/\eta_0$  is currently under study.

Due to the higher density of the pores in the samples studied, their maximum efficiency is 2-8 times greater than the maximum efficiency of the corresponding N005 and N003 polycarbonate filters of the Nucleopore type [16, 17]. This characteristic can be improved by increasing the pore density and decreasing the film thickness.

We would like to thank Academician G. N. Flerov for his continuous attention to the study. We would also like to thank N. V. Karzhavina for assisting in the measurements of the maximum efficiency and A. Yu. Didyk for irradiating the films with the ions.

#### LITERATURE CITED

1. P. B. Price and R. M. Walker, J. Appl. Phys., **33**, 3407 (1962).
2. G. N. Flerov and V. S. Barashnikov, Usp. Fiz. Nauk, **114**, No. 2, 351 (1974).
3. C. P. Bean, M. V. Doyle, and G. Entine, J. Appl. Phys., **41**, 1454 (1970).
4. J. A. Quinn, J. L. Anderson, W. S. Ho, and W. J. Petzny, Biophys. J., **12**, 990 (1972).
5. R. E. Beck and L. S. Shultz, Biochim. Biophys. Acta, **255**, 273 (1972).
6. B. V. Mchedlishvili, S. E. Bresler, V. M. Kolikov, V. M. Kolodkin, G. N. Flerov, V. S. Barashnikov, S. P. Tret'yakova, V. A. Shchegolev, T. I. Kozlova, T. A. Aksenova, and M. B. Korolev, Kolloidn. Zh., **40**, No. 1, 59 (1978).
7. L. N. Bryzgalov, N. S. Zhukovskaya, and L. A. Kukhina, in: Production, Properties, and Use of Plastics and Articles Made from Them [in Russian], NIITEKhim, Moscow (1977), p. 152.
8. W. T. Crawford, W. DeSorbo, and J. S. Humphrey, Nature, **220**, 1313 (1968).
9. P. Yu. Apel, Nucl. Tracks, **6**, No. 2/3, 115 (1982).
10. S. P. Tret'yakova, P. Yu. Apel, L. V. Jolos, T. I. Mamonova, and V. V. Shirkov, in: Proceedings of the 10th International Conference on Solid State Nuclear Track Detectors, Pergamon Press, Oxford (1980), p. 283.
11. P. Yu. Apel' and S. P. Tret'yakova, Prib. Tekh. Eksp., No. 3, 58 (1980).
12. A. M. Hindelch and D. J. Johnson, Polymer, **19**, No. 1, 27 (1978).
13. B. V. Mchedlishvili and V. M. Kolikov, in: IV Conference on the Use of New Nuclear Physics Methods for Solving Scientific-Technical and Economic Problems, Joint Institute of Nuclear Research R18-82-117, Dubna (1982), p. 139.
14. B. V. Deryagin, B. V. Zheleznyi, Z. M. Zorin, V. D. Sobolev, and N. V. Churaev, in: Surface Forces in Thin Films and the Stability of Colloids [in Russian], Nauka, Moscow (1974), p. 90.
15. Z. M. Tobina, in: Studies in the Field of Surface Forces [in Russian], Nauka, Moscow (1967), p. 24.
16. V. P. Dubyaga, E. E. Katalevskii, and L. P. Perepechkin, in: Polymer Membranes [in Russian], Khimiya, Moscow (1981), p. 222.
17. Nucleopore Filtration Products for the Laboratory, Catalog Lab 50, Pleasanton, California (1980), p. 26.